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(54) **Improved tire tread adhesives.**

(57) **A tire tread cement comprising a water-in-oil emulsion having as its oil phase an organic solvent solution of a vulcanizable rubber compound.**

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This invention relates to the development of an adhesive having a very low level of volatile hydrocarbon. It has particular utility for bonding a tire tread to the carcass or casing.

5 The key requirements for tread adhesive in the tire industry are: good green tack, good cured adhesion and fast drying time. Tread adhesives, also referred to as tread cements in the industry, are employed in the tire-building stage to bind green tread to green tire
10 carcass or, in case of retread tires, to tire casing. There are two types of tread adhesives, namely tread bottom (or "undertread") and tread end (or "splice") adhesives.

 These adhesives are applied to the tread while
15 the tread stocks are being made, as follows: as a strip of tread is being extruded (at a temperature between 200 - 250° F.) the tread bottom adhesive is continuously applied to the bottom part of the hot tread, generally by a roller or a brush. After the adhesive solvents evaporate,
20 the tread is passed through water tanks for cooling. Afterwards, the tread is dried, skived (meaning cut on an angle into small pieces), coated with a tread end adhesive, and stored in a tread tray. The time required for the tread to travel from the exit end of the extruder
25 to the water tanks is called scorch time, usually less than a minute. Therefore, any adhesive should dry sufficiently within this scorch time to the extent that the adhesive will not wash off the extruded tread in the cooling tanks.

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Commercial tread adhesives employ a large amount of volatile hydrocarbon as solvent. Because of environmental regulations, volatile hydrocarbon solvents are deemed undesirable except in limited quantity.

5 Reductions of hydrocarbon emission from the adhesives could be achieved if the hydrocarbon solvent is partially replaced or diluted with water. Consequently a water-base adhesive could be an approach in developing adhesives with low levels of hydrocarbon emission and the
10 achievement of this is also one of the primary objects of the invention.

THE INVENTION

A tire tread cement comprising a water-in-oil emulsion having as its oil phase an organic solvent solution of a vulcanizable rubber compound.
15

I. The Organic Solvent of the Vulcanizable Rubber Compounds

A. The Vulcanizable Rubber Compound

The vulcanizable rubber compound includes an unvulcanized natural or synthetic rubber (e.g., Buna,
20 SBR, etc.) combined with a cross-linking system and other compounding ingredients. Preferred is a tread stock rubber compound, since there can be no question that it will be compatible with the tread rubber of the tire. There are many equivalents. The amount present in
25 the emulsion will vary between 0.5 to 15 and, preferably, 1 to 10% by weight.

B. The Organic Solvents

The invention utilizes as the organic solvent an organic hydrocarbon liquid which has a boiling point
30 at least 10° F. greater than the boiling point of water. Such solvents may be selected from a wide variety of materials. One such material may be designated as a low odor paraffin solvent, LOPS. This solvent has the fol-

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lowing characteristics:

	Specific Gravity 60°F.	0.780 - 0.806
	Color, Saybolt	+ 30 min.
	Appearance, visual	Bright and Clear
5	Aniline Point, °F., ASTM D-611	160 min.
	Distillation, °F., ASTM D-86	
	IBP	365 min.
	FBP	505 max.
10	Flash Point, °F., TCC	140 min.
	Sulfur, ppm, Micro- coulometer	15 max.

In addition to using these paraffin-type solvents which are preferred, it is understood that other solvents such as high boiling kerosenes, naphthas, lubricating stocks, mineral spirits, and the like may be used.

While these high-boiling solvents may be used alone with the vulcanizable rubber compound to provide the oil phase of the water-in-oil emulsion, such requires that the tire tread stock so treated with such emulsions be subjected to extensive drying times. To speed up the drying time, it is a preferred embodiment of the invention to use as organic solvent solvents of the type described above in combination with low boiling solvents.

Low-boiling solvents are organic liquids, preferably hydrocarbon organic liquids, which have a boiling point below 111°C. Typical of such solvents are gasoline, hexane, heptane, toluene and the like. When these low-boiling organic solvents are combined with the high boiling organic solvents, it is preferred to do so to provide a ratio of high boiling solvent to low boiling solvent within the range of 5:1 to 1:5. The particular ratio embodied will be governed by the ingredients of the finished emulsion, the rubber stock being treated, and the drying environment to which the emulsion would be subjected.

When a higher level of solvent emissions can be

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tolerated, solvents used to make up the oil phase of water-in-oil emulsions can consist entirely of low-boiling organic liquids such as those enumerated above.

II. Ratio of Organic Solvent to Water

5 To make satisfactory emulsion, it is desirable that the ratio of organic solvent to water be within the range of 1:5 to 4:1. In most instances, good products are afforded when the ratio is 1:1 to 1: 3.5. Again, the ratios must be adjusted to suit the use to which the par-
10 ticular products are employed.

In the emulsion, the organic solvent is present by weight in amounts ranging from 1 - 50 and, preferably 5 - 40% by weight.

III. The Surfactant - Water-in-Oil Emulsifier

15 One of the surprising features of the invention is that the emulsions used in the invention are rendered stable by utilizing a surfactant which has an HLB within the range of 8-18 and preferably 8-14.

Emulsifiers may be classified by using the Atlas
20 HLB System. This system is described in the publication entitled, The Atlas HLB System, 4th Printing, Atlas Chemical Industries, Inc., Wilmington, Delaware, 1963. This publication and its entire contents are incorporated herein by reference and made a part of this specifica-
25 tion. Generally, oil-soluble emulsifiers produce water-in-oil emulsions, whereas water-soluble emulsifiers produce oil-in-water emulsions.

Also, as a general rule, the HLB number of the oil-soluble emulsifier will range between 4-9, whereas
30 the HLB number of the water-soluble surfactant or emulsifier will have a value of approximately 8 - 40. In certain cases, a single surfactant may be capable of producing either a water-in-oil or oil-in-water emulsion.

Surfactants within the HLB range of 8 - 18 are
35 normally considered as oil-in-water emulsifiers, yet they act as water-in-oil emulsifiers for the emulsions used in

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the practice of this invention. A preferred surfactant is the material known as Polytergent B-150, which is a nonylphenoxy polyethoxyethanol having an HLB of 8.8.

It is further characterized as dispersible, but not soluble in water. Another useful material is Triton X-114 which is octylphenol reacted with about nine moles of ethylene oxide. It has an HLB of 12.5

Other water-dispersible or -soluble surfactants falling within the above parameters may be used.

10 While surfactants of the above type are preferred, it is understood that low HLB surfactants may be used to stabilize the emulsions.

The amount of surfactants used to produce the water-in-oil emulsions of the invention may be varied
15 between as little as 0.05 up to 10% by weight with a preferred range being 0.1-5% by weight. The exact amount is, of course, dependent upon the emulsifier used in the ingredients of the emulsion and the like.

IV. Additional Ingredients

20 A. Tackifiers

It is common to employ in the formulas of the invention tackifiers which aid in developing the tackiness of the vulcanizable rubber compound. Materials of this type are well-known to the art. A typical material of
25 this type is sold under the trademark AKROCHEM P-90. This material is an alkylphenol formaldehyde resin. The tackifiers may be used in the formulation in amounts ranging between 1-10% by weight with a preferred range being 2-5% by weight. Another method of calculating tackifier dosage is to use an amount ranging between the weight
30 ratios of 0:1 to 8:1 based on the vulcanizable rubber compound. From these ratios is apparent the tackifier is an optional ingredient.

B. Plasticizers

35 A plasticizer for the rubber compound is used to enhance the cured adhesion and since its boiling point is

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extremely high, it should remain effective for weeks without appreciable loss due to evaporation. Coated on a hot green tread, this tackifier should also increase the green tack of the tread adhesive and should also serve the role of an nonvolatile solvent. The preferred plasticizer, Santisizer 97, heptyl nonyl adipate ester. The amount of plasticizer when this ingredient is used may vary between 1-10% by weight.

V. Breaking the Emulsions

Another surprising feature of the invention is that the emulsions break under conditions of use. Specifically, they break when they come in contact with uncured rubber, either natural or synthetic. This deposits the adhesive on the surface treated with the emulsion. Subsequent drying removes the excess water and low boiling organic solvent, if such is present. The high boiling organic solvent is absorbed into the rubber, thereby increasing its tackiness. This improves the adhesive characteristics of the total assemblage treated with the adhesive.

VI. General Formula

To illustrate the invention more specifically, a general formula is set forth below:

<u>General Formula</u>		
	<u>Ingredients</u>	<u>% by Weight</u>
25	Rubber Compound	
	General	.5-15
	Preferred	1.0-10
30	The Organic Solvent	
	General	1.0-50
	Preferred	5.0-40
	Water	
	General	10.0-80
	Preferred	20.0-75

The Surfactant		
	General	0.5-10
	Preferred	0.1- 5
Tackifier		
5	General	0.0-10
	Preferred	1.0- 5
Plasticizer		
	General	1.0-10
10	Preferred	1.0- 0

To further illustrate the invention, the following are presented by way of examples.

EXAMPLES

Example 1

15 With the foregoing in mind, the following formulation (water-in-oil emulsion adhesive) was developed having a low order of hydrocarbon content (hydrocarbon content reduced by 88.3%) and when tested against an industry standard (hydrocarbon based solvent), the emul-
 20 sion adhesive equaled the standard on the basis of cured adhesion but was deemed somewhat inferior in green tack strength. Nonetheless, this adhesive did demonstrate the feasibility of preparing a tread adhesive with a low level of hydrocarbon.

25 Composition 1

		<u>Wt. %</u>
	Rubber Compound (Natural rubber-based tread stock)	8.69
30	Heptane	10.86
	Tackifier (1)	3.80
	LOPS	40.82
	Plasticizer (2)	5.30

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Surfactant	1.19
H ₂ O	<u>29.34</u>
	100.00

5 (1) Akrochem P-90: alkyl phenol formaldehyde
condensation product

(2) Santisizer 97

The rubber compound is a natural rubber tread stock. This is also true of the rubber compound in the examples following. A preferred rubber compound is one
10 having a Mooney (ML) Viscosity of 32 to 54; Shore "A" hardness 55/69; 100% modulus, 250/350; 200% modulus, 600/1100; tensile, 310/500.

This emulsion has a Brookfield viscosity of 3200 (#3 spindle, 12 RPM). A 2 mil coating of this adhesive
15 applied to a hot green tread (heated with hot air at 200 - 200°F. for 40 seconds) will dry in about one minute. The emulsion adhesive, however, was found to be unstable to further addition of water in an effort to reduce its solids content. To overcome this deficiency, a second
20 formulation was tried (Example 2) having a water content of 41.5% and 9.5% solids. It was found this adhesive could be further diluted with water to contain only 3.8% solids, 77% water, without encountering emulsion instability.

25 Example 2

Another composition was prepared and tested. Its formula is set forth below as Composition 2:

Composition 2

	<u>Wt. %</u>
30 Isoprene-SBR-Based Rubber Compound	2
Tackifier (above)	6
Heptane	10
LOPS	30

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Plasticizer (abov l	10
Surfactant (above)	0.5
H ₂ O	<u>41.5</u>
	100.0

- 5 Attributes and features of this example on further dilution are set forth in Table 1.

TABLE I

	Comp. 2		Comp. 2		Comp. 2		Standard Cement %
	%	H ₂ O (1:1)	H ₂ O (2:3)	H ₂ O (2:3)	H ₂ O (6.5:3.5)	Rubber compounds dissolved in gasoline	
Rubber Compound	2	1	0.8	0.7			
Tackifier	6	3	2.4	2.1			
Heptane	10	5	4.0	3.5			
LOPS	30	15	12.0	10.5			
Santizer 97	10	5	4.0	3.5			
Polytergent B-150	0.5	0.25	0.2	0.17			
H ₂ O	41.5	70.75	76.6	79.53			
	100.0	100.0	100.0	100.0			
Emulsion stability 1 week standing	no separation	no separation	no separation	no separation			no separation
Green Tack (PSI), 2 mil	Fresh 5 days	7.4 6.2	5.0 3.8	6.4 3.1	6.0 2.1		4.0 3.9
Cured Adhesion, 2 mil							
Tensilo (psi)	cold (1) hot (2)	175 63.6	203 75.0	210 06.7	107 72.5		173 75.0
% Cohesive Failure	cold hot	100 100	100 100	100 100	100 100		100 100
Bks cps 24°C, 12, 30 RPM		45.6	290	210	200		25.0
(1) Tested at Ambient Temperature							
(2) Tested at 250°F							

(1) Tested at Ambient Temperature
(2) Tested at 250°F

TABLE I (Continued)

<u>% Hydrocarbon emission on rubber</u>	Comp. 2	Comp. 2	Comp. 2	Comp. 2	Standard
	<u>%</u>	H ₂ O (1:1) <u>%</u>	H ₂ O (2:3) <u>%</u>	H ₂ O (6.5:3.5) <u>%</u>	Cement <u>%</u>
	28.8	13.0	10.0	—	89.2
<u>% Emission Reduction</u>	67.7	85.4	88.8	—	—
<u>Drying Time at 200-220°F, 2 mil</u>	Less than 40 sec.	Less than 40 sec.	Less than 40 sec.	—	5 sec.

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Example 3

Another composition was prepared. This one utilized a harder rubber compound:

Composition 3

5		<u>Wt. %</u>
	Polyisoprene	
	Rubber Compound	1
	Akrochem P-90	3
	LOPS	15
10	Santisizer 97	5
	Polytergent B-150	0.25
	Heptane	5
	H ₂ O	<u>70.75</u>
		100.00

15

Physical Properties

Brookfield viscosity: 650

(#2 spindle, 30 rpm, 25°C)

Flash point (°F) - 64

Laboratory tests showed that the performance properties of Composition 3, including cured adhesion and green tack, were comparable to those of Composition 2 diluted with an equal weight of water.

Example 4

In this Example, a soft rubber compound was chosen for use in a preferred composition as described below. Compositions 3 and 4 were compared against each other in field tests conducted at different tire companies:

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Composition 4

		<u>Wt. %</u>
5	Natural rubber-based Rubber Compound (Mooney ML 32)	1
	LOPS	14
	Akrochem P-90	4
	Santimizer 97	5
	Polytergent B-150	0.25
10	Heptane	5
	H ₂ O	<u>70.75</u>
		100.00

Physical Properties

- Brookfield viscosity: 1500
 (#3 spindle, 30 rpm, 26°C)
 % solids: 8.8% moisture balance, 15 min.

As a result of a successful field test with Example 3 on tread bottoms, the adhesive was characterized by the tire manufacturer as five to six times better in green tack compared to a hydrocarbon based cement. Even after standing for seven days, a tread coated with the cement could be used to build a tire without the need for wiping the surface of tire carcasses with a solvent for rejuvenation of the tread cement.

Some tires were also built for experiment using the adhesive of Composition 4, tested for endurance. The adhesive was used both as an undertreat and a tread end cement. The tires set a new record in mileage before failure under the endurance test. A further field test revealed superior green tack and treads coated therewith still had sufficient green tack for tire building after standing for nine days.

It was also determined on an experimental basis there was no noticeable difference between application of the two formulations (Composition 3, Composition 4) to

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tread surfaces. Both were easily brushed on and the emulsions easily broke, allowing the water to be brushed off or blown off with air. The treads were allowed to stand (age) for two hours before building the tires. The green tack of Example 3 was deemed equal to the standard hydrocarbon cement. The green tack of Composition 4 was found to be far superior to the standard, so much so that the tire builder had difficulty adjusting the tread on the carcass (usually necessary), further evidencing efficacy of this formulation as an end splice cement.

From the standpoint of cured strength, tires built with the adhesive of Composition 4 exceeded the endurance standards both of the manufacturer and the Department of Transportation.

As the solvents evaporate, the increasing proportion of water renders the emulsion more and more unstable, heat and/or pressure will easily break the unstable emulsion, and the active ingredients are released to bond the two surfaces.

Laboratory tests indicate that the performance properties of Composition 4 were comparable to those of Composition 3.

In general, water-based tread cements can be applied to green treads by brushing, spraying, or roller coating. Suitable techniques of the cement coating for tire building range from about 2 to 4 mils. When the coating is applied to the green tread at thicknesses which are too thin, the green tack of the aged tread may be insufficient for tire building. When the coating is applied too thick, the cement may not dry within the scorch time.

Example 5

Listed below are additional compositions of the invention designated as Compositions 5 and 6. These compositions illustrate that the ratio of tackifier to rubber may be varied yet, at the same time, still provide good adhesive compositions:

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		Composition 5	Composition 6
		<u>Wt. %</u>	<u>Wt. %</u>
	Natural rubber-based		
	Rubber Compound	1	1
5	Akrochem P-90	1	6
	LOPS	17	12
	Santisizer 97	5	5
	Polytergent B-150	0.25	0.25
	Heptane	5	5
10	H ₂ O	<u>70.75</u>	<u>70.75</u>
		100.00	100.00

The performance properties by laboratory tests of the Compositions 5 and 6 were similar to those of the Composition 3.

15 Example 6

Listed below are Compositions 7 and 8. These compositions show that different emulsifiers may be used to provide compositions of the invention. In the following formula, Triton X-15 is octyl phenol reacted with a few moles of ethylene oxide. It has an HLB of 3.6

		Composition 7	Composition 8
		<u>Wt. %</u>	<u>Wt. %</u>
	Natural rubber-based		
	Rubber Compound	1	1
25	LOPS	14	14
	Akrochem P-90	4	4
	Santisizer 97	5	5
	Surfactant		
	Triton X-114	0.25	0.25
30	Triton X- 15		
	Heptane	5	5
	H ₂ O	<u>70.75</u>	<u>70.75</u>
		100.00	100.00

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Both cured adhesion and green tack of the Compositions 7 and 8 were comparable to those of Example 3 by laboratory tests.

Example 7

- 5 An example of a good water-based adhesive is set forth below as Composition 9:

<u>Composition 9</u>		<u>Wt. %</u>
10	Natural rubber-based Rubber Compound	1.36
	Akrochem P-90	8.15
	LOPS	4.08
	Toluene	15.41
	Polytergent B-150	0.25
15	H ₂ O	<u>70.75</u>
		100.00

Brookfield viscosity (#3 spindle, 30 rpm, 22°C.) - 1560 cps.

Having thus described our invention, we claim:

CLAIMS

1. A tire tread cement comprising a water-in-oil emulsion having as its oil phase an organic solvent solution of a vulcanizable rubber compound.

2. The tire tread cement of Claim 1 where the organic solvent is a blend of high boiling point and low boiling point organic solvents combined in a ratio of 1:5 to 5:1.

3. The tire tread cement of Claim 1 wherein the water-in-oil emulsion contains a surfactant having an HLB between 8-18 and is capable of stabilizing the emulsion.

4. The tire cement of Claim 1 wherein the water-in-oil emulsion contains an emulsifier having an HLB value of between 4-9.

5. The tire tread cement of Claim characterized in that it contains a tackifying agent.

6. The tire tread cement of Claim 4 where the ratio of tackifying agent to vulcanizable rubber compound is within the range of 0:1 to 8:1.

7. A tire tread cement comprising:

<u>Ingredients</u>	<u>% by Weight</u>
Rubber Compound	
General	0.5-15
Preferred	1.0-10
The Organic Solvent	
General	1.0-50
Preferred	5.0-40
Water	
General	10.0-80
Preferred	20.0-75
The Surfactant	
General	0.5-10
Preferred	0.1- 5
Tackifier	
General	0.0-10
Preferred	1.0- 5

<u>Ingredients</u>	<u>% by Weight</u>
Plasticizer	
General	1.0-10
Preferred	1.0- 0

8. In a method of forming tires wherein tread stocks are joined to a green tire carcass or tire casing, the improvement comprising utilizing as the tread adhesive a composition comprising:

<u>Ingredients</u>	<u>% by Weight</u>
Rubber Compound	
General	0.5-15
Preferred	1.0-10
The Organic Solvent	
General	1.0-50
Preferred	5.0-40
Water	
General	10.0-80
Preferred	20.0-75
The Surfactant	
General	0.5-10
Preferred	0.1- 5
Tackifier	
General	0.0-10
Preferred	1.0- 5
Plasticizer	
General	1.0-10
Preferred	1.0- 0